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1. INTRODUCTION

Accurate quantification of certain gases in the blood stream and in the expired air can give vital information for trauma care and diagnosis of the malfunction of a number of organs. CO_2 , O_2 and NO are three important gases reflecting human physiological conditions. Continuous monitoring of these gases can provide vital information of shock and subsequent resuscitation. A sensor capable of continuously monitoring these gases can be integrated into a self-contained life sustaining unit like the trauma pod.

Currently existing gas sensing technologies include chemiluminescence, mass spectrometry, gas chromatography, infrared absorption spectroscopy, surface Raman scattering and others. Most of these current detection technologies rely on selective chemical reaction of the gas being detected with another reactant. However, the existence of a gas of similar chemical nature interferes the detection especially when this interfering gas is present in much larger concentration. One very severe practical limitation is the interference due to the water vapor molecule which is almost always present in a biological system. Other non-chemical methods that rely on surface interaction have major drawbacks of over sampling contamination and slow response. Other more chemically selective techniques such as gas chromatography and mass spectrometry and their combinations require sophisticated instrumentation and professional care for maintenance and have short maintenance cycle. These limitations call for a compact chemically selective gas detection system that can detect different gases simultaneously without interference by other species.

Research in Division of Surgery, Walter Reed Army Institute of Research (WRAIR) have shown that the decompensatory phase of hemorrhagic shock can be slowed by the inhibitors of NO production. Thus, measurement of NO levels in the expired air will provide vital information on trauma care and effectiveness of the resuscitation effort. At present there is no reliable technique for measurement of the NO levels in the expired air. Similarly, inadequate tissue perfusion during hemorrhagic shock results in a decrease of oxidation metabolism and diminished whole body oxygen consumption and carbon dioxide production. For that reason, continuous monitoring of CO_2 and O_2 levels in the expired air will give information on the level of the hemorrhagic shock and the success of resuscitation effort. At present, there is no system that measures the levels of O_2 and CO_2 simultaneously in the expired air. A small laboratory system for the purpose of research in this field is urgently needed. The results of the research will lead to the development of a miniaturized version which can be used in the field.

Most of the current high sensitivity laser absorption spectrometers are based on tunable diode lasers and these instruments, to date, have been fairly bulky and expensive laboratory type of developmental systems. Princeton Electronic Systems (PES) has developed a diode laser based measurement technique which can monitor the levels of various gases in the expired air as well as in the blood stream. The technique can monitor gases up to parts-per-trillion level and since it is based on diode laser spectroscopy, the sensors can be miniaturized so that eventually they can be put inside small airway catheters. The technique has been demonstrated in our

laboratory. In this Phase I program we had proposed to construct a compact room temperature diode laser based system for monitoring biologically important gases such as O₂, CO₂, etc. By using compact thermal electric cooler and start-of-the-art electronic integration technology, ultimate size of system can be made smaller than a soda can. The most important objective of this program was to fabricate a field portable prototype detection system for measuring O₂ in human expired air. Once this prototype is built using off-the-shelf components, further miniaturization can be undertaken. The system will be miniaturized in Phase II and simultaneously monitoring multiple species will also be conducted in that program.

2. DIODE LASER FREQUENCY MODULATION SPECTROSCOPY

2.1. Chemically Selective Sensitive Trace Gas Detection via Infrared Diode Laser Absorption Spectroscopy

Most gas molecules possess an infrared (IR) absorption spectrum which is sufficiently distinct to allow identification and discrimination among several species. Provided the transition is strong enough for each of the species of interest, IR absorption could thus form the basis for versatile, sensitive trace gas detection system. Table 1 lists some of the detectable molecules and the suitable absorption bands.

| Gas | Absorption Band Center(cm ⁻¹ /mm) | Sensitivity* | Ultimate Sensitivity* | Laser Type |
|-------------------------------|--|--------------|-----------------------|------------|
| ¹² CO ₂ | 4977.875/2.01 | 0.2 ppmv | 46 pptv | III-V |
| ¹³ CO ₂ | 4887.391/2.05 | 20 ppmv | 0.46 pptv | III-V |
| O ₂ | 13120.909/0.762 | 24 ppmv | 5.4 ppbv | III-V |
| NO [†] | 1875.972/5.33 | 0.725 ppbv | 0.17 pptv | lead-salt |
| NO [‡] | 3723.853/2.685 | 43 ppbv | 10 pptv | III-V |
| H ₂ O | 7249.811/1.379 | 8.63 ppbv | 2 pptv | III-V |

Table 1. Detectable species and the corresponding absorption bands. *Sensitivity are determined using 7 cm optical pathlength, 1Hz detection bandwidth and a routinely achievable 5x10⁻⁷ absorbance limit; ultimate sensitivity are determined using 30 m optimum optical pathlength, 1 Hz detection bandwidth and a laboratory established 5x10⁻⁸ absorbance limit.¹

[†]Ultrahigh sensitivity lead-salt laser unit which requires cryogenic cooling for the laser. [‡]Laser diodes are available in some research end products.

2.2. Tunable Diode Lasers

Semiconductor diode laser technology makes possible the fabrication of single wavelength, tunable light sources, which can be designed to emit light at a specific wavelength. The tunability of all semiconductor lasers is based on the concept of band gap tuning in which the band gap energy and hence lasing frequency is adjusted by appropriate alloy composition of the compound semiconductor. These sources are well matched to sensitive detection requirements. They have very narrow band of emitted radiation, emit high enough laser intensity to allow quantum limited detection.¹⁻³ and can be easily frequency and wavelength modulated through the laser injection current.⁴ The latter feature is especially important when considering signal processing requirements.

The most versatile semiconductor technology for tunable laser sources is based on lead-salt semiconductors. These devices cover the 300 cm^{-1} to nearly $3,000\text{ cm}^{-1}$ ($3.3\text{-}30\text{ }\mu\text{m}$) spectral range. However, these lasers require being operated at cryogenic temperature and cause temperature controlling difficulties in the field. Using III-V compounds, room temperature diode lasers are available upto $3.4\text{ }\mu\text{m}$. Near room temperature diode lasers are available upto $2.4\text{ }\mu\text{m}$. These advanced lasers can be operated with thermoelectric coolers and simplifies the operation and permits fabrication of portable systems based on these lasers.

2.3. Frequency Modulation Diode Laser Spectroscopy

In order for diode laser absorption spectroscopy to be used in a sensitive chemical detection device, it is necessary to overcome some attendant difficulties in measuring the amount of light absorbed. Indeed the central difficulty is that even for relatively strong absorption lines,² little laser light will be absorbed and if one simply measures transmitted laser power through an absorbing gas, a host of noise sources will obscure the small reduction in transmitted light that the absorption causes. This limitation may be surmounted by employing a technique known as frequency modulation (fm) spectroscopy^{2,3} wherein the laser frequency is modulated at rf frequencies. When the laser is tuned through a spectrally narrow feature, the fm light is converted to amplitude modulated light and the amplitude modulation may be measured with much higher sensitivity than the directly absorbed light. This approach allows the detection of absorbance as small as a few parts in 10^8 .^{1,3}

Due to this high sensitivity, in almost all situations, false absorption features are detected as well.^{2,5-7} These false features, especially transparent optical surface generated interference fringes, could be 2 to 3 orders of magnitudes higher than the theoretical limits.⁵⁻⁷ This sensitivity limiting false features has been the practical sensitivity limiting factor for more than a decade.⁵ Using another level of low frequency triangular wave modulation,⁵ molecular absorption features can be separated from the false absorption features.⁷ The overall modulation technique is especially well suited for use with diode lasers as their frequency may be modulated directly through the injection current.

Figure 1 shows the basic principle of diode laser frequency modulation spectroscopy technique. The laser frequency modulation is conducted through the modulated laser injection current. When the modulated light passes through the absorption cell, the cumulated absorption signal mixes with the modulated light signal in a special manner. After the detected signal is demodulated by a lock-in amplifier, the undesired noise picked-up in the detection process is significantly suppressed and the desired absorption signal is transferred into the data acquisition system.

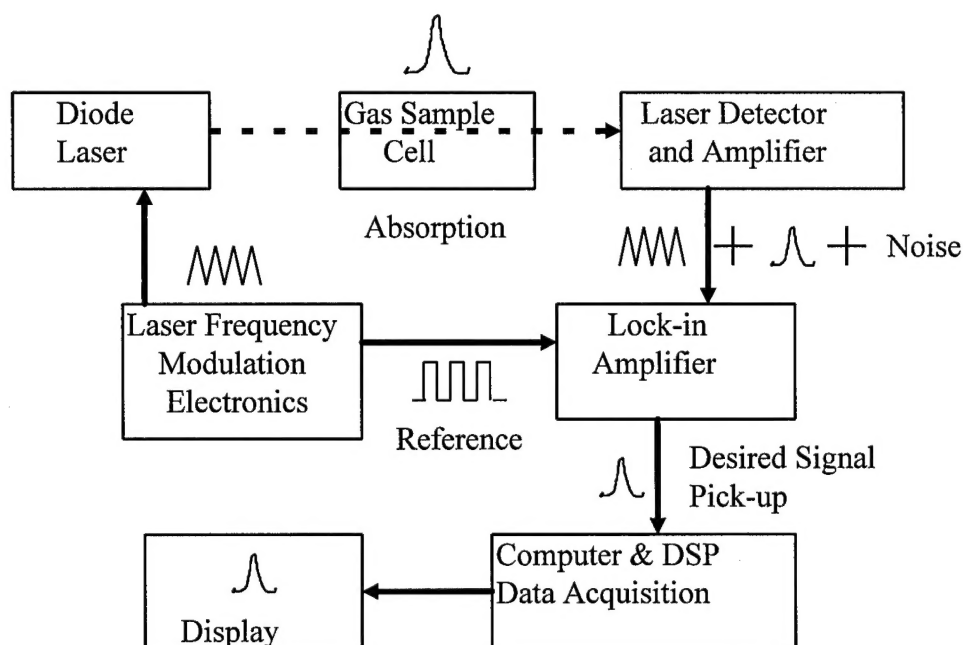


Figure 1. The basic principle of diode laser frequency modulation spectroscopy.

3. PROPOSED WORK AND WORK PERFORMED

3.1. Proposed Work

In Phase I, we proposed to construct a bench-top portable O₂ monitor prototype as well as achieving a high accuracy detection of O₂ in the expired air. Based on the theoretical data of O₂ absorption bands in the infrared spectral region from the HITRAN database and the experimental data of O₂ detection⁸, the O₂ absorption band at the 762 nm wavelength region has the strongest

absorption lines in the whole infrared region. Therefore, a diode laser from Mitsubishi which emits light at 758-762 nm was selected as a light source in this program.

3.2. Work Performed

The gas monitor design is based on the frequency modulation spectroscopy scheme. The simplified schematic diagram of the technique is shown in Figure 2. The major modules are the current source, the laser head, the gas absorption cell, frequency modulation source and the detector-demodulator module. In the design, the laser head is integrated to the gas cell. The triangle wave function generator is integrated with the laser current driver module into one circuit board. The laser detector and a preamplifier are integrated into one small block.

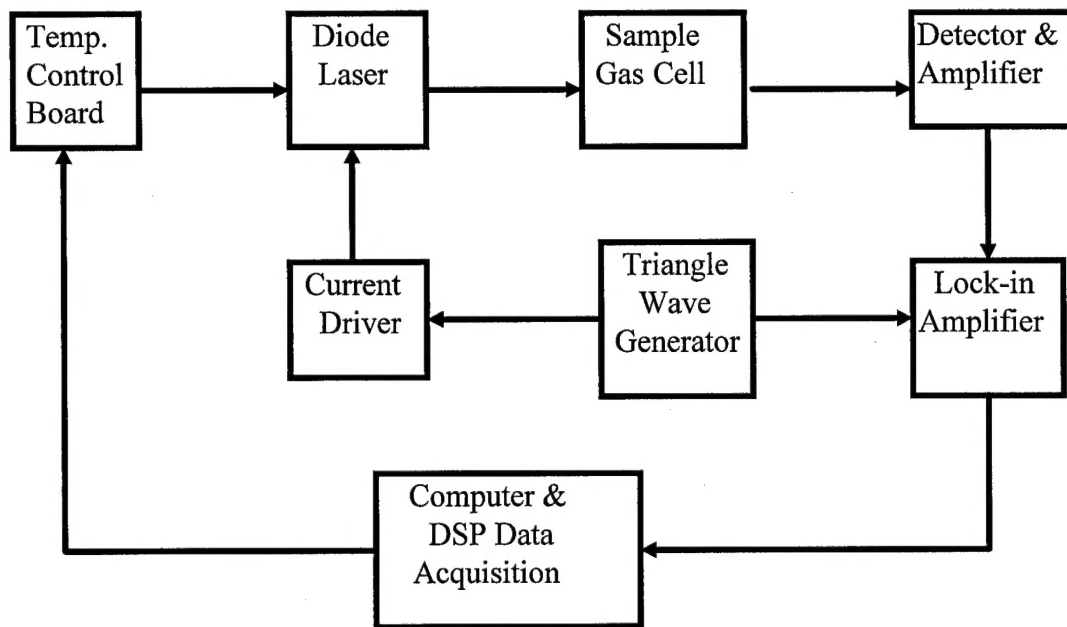


Figure 2. The schematic diagram of frequency modulation spectroscopy.

3.2.1. Instrumentation Size Reduction from the Previous Version

Based on our new system designs, the whole monitor prototype size has been significantly reduced from the previous module (9"x14"x17") to the new module (5"x14"x17"). Further one third volume reducing is possible by redesigning a new gas cell and electronic systems. Our final

goal in this phase II and the following phase program is to construct a hand-held medical gas sensor with high detection accuracy.

3.2.2. System Power Supply

Power consumption components in the system are the single board computer, DSP board, TEC temperature controller board, cooling fans, a gas pump, the laser current driver, electronics, etc. The DC power supply (± 12 V, ± 5 V, and 3V) is converted from regular AC power supply. The total consumption power of the system is about 30 W. In order to reduce the residual noise level of power supply for the electronic circuit parts, the re-regulation of DC power output is taken inside the system.

3.2.3. Laser Current Source

Diode lasers require stable current sources to operate. To implement the frequency modulation spectroscopy, the current source must be able to modulate the laser driving current in a high frequency. Currently, modularized current source based on hybrid circuits are available commercially. Different diode lasers require current source capable of delivering current ranging from 50 mA to 2 A. We have acquired several modular current sources that fit our requirements and have full load current output of 100mA, 200mA and 1A, respectively. For the specific laser employed in this monitor (the operating current of 49 mA is required), the driver module with the 100 mA current output is used. The physical size of the module is 1.5"x2.5"x3/4".

3.2.4. Temperature Controller

The wavelength of diode lasers is very sensitive to the laser temperature change. In order to well control the laser wavelength, i.e., to stabilize the laser spectral performance, the temperature of the laser has to be properly locked. The temperature controller for thermoelectric coolers has been developed by us using hybrid circuits. The overall circuit integrates a 2A dual polarity current source and a close loop control circuit which utilizes a thermister as the temperature sensors. The space required is 2.5"x2.5"x1" and our test indicates a power consumption from 300 mW to 4 W depends on the temperature control requirement of the particular diode laser used.

3.2.5. The Gas Cell

The gas cell has a demanding set of mechanical and electrical specifications. We used low cost off-the-shelf ultra-high vacuum components for its development. The laser and detector mounts were tailor-made to suit this application. The cell integrates a 8 pass optical cell (10 pass maximum), the laser head and the photodetector for base performance. Commercially available cell costs as much as \$20k. Our current design costs about \$500. Figure 3 is photograph of the first prototype of this cell. The length of the cell is 5". There are a miniature pressure sensor and a miniature electronic gas flow valve which are connected to the cell. In phase II, we will redesign a miniature gas cell for a hand-hold purpose.

3.2.6. The Laser Frequency Modulation

The diode laser frequency modulation spectroscopy is an advanced absorption detection technique. In order to achieve high sensitivity detection, the out-of-phase (π -phase difference) sidebands have to be generated, i.e., the laser light has to be *frequency* modulated. With a diode laser as light source, the frequency modulation can be easily conducted by modulating the laser injection current. In this detection scheme, a triangle waveform, which is generated internally, is applied to achieve the diode laser frequency modulation.

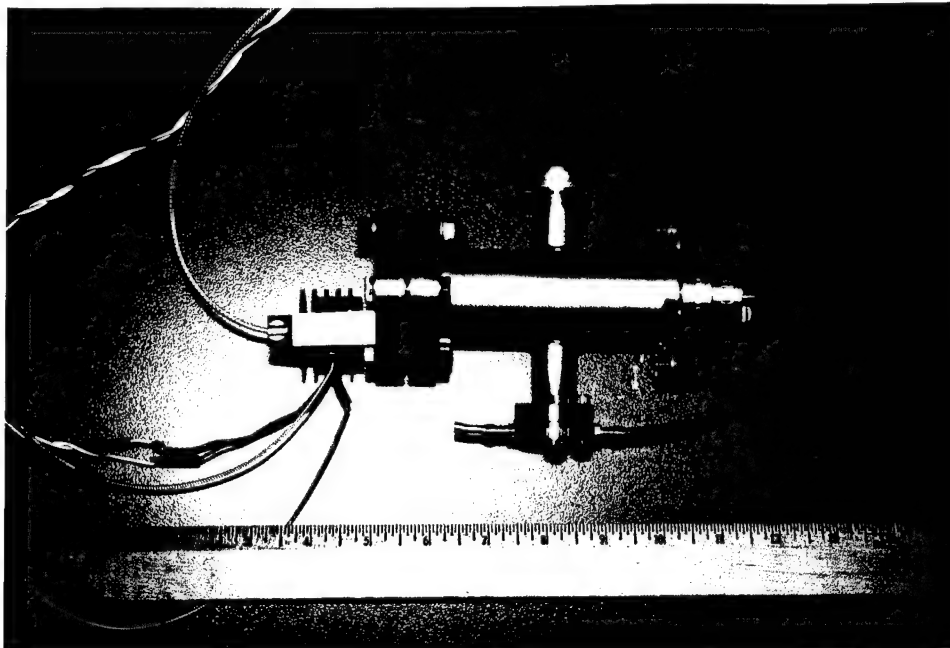


Figure 3. The prototype of 10-pass sample gas cell.

3.2.7. The Detector-Demodulator Module

The performance of this module is very important to the detection sensitivity of the overall detection scheme. This module includes a high frequency photodetector, signal preamplifier, a lock-in amplifier, and a digital signal processor. The photodetector and the signal preamplifier were integrated in a single circuit board of 0.5"x1". The photodetector and the preamplifier were then integrated to the gas cell for minimum disturbance and maximum RF shielding.

The output of the preamplifier is fed to a lock-in amplifier. PES has designed and fabricated a compact lock-in amplifier that has a bandwidth of up to 1 MHz. The digital signal processor is an off-the-shelf DSP board based on Texas Instrument TMS320C31 33 MFLOP (50 MFLOP enhancement available) signal processor which consumes only 1 W of power. The DSP performs signal averaging and frequency modulation-demodulation in addition to the detection

scheme. It also leaves room for high performance post spectrum acquisition signal enhancements once the enhancement algorithms are available.

3.3. The O₂ Detection and the Detection System Performance Specifications

As mentioned early in this report, O₂ molecule has the strongest absorption band in the 762 nm spectral region. By selecting this absorption band for detecting the oxygen, the absorption pathlength can be shorter without sacrificing sensitivity loss compared to selecting a weak absorption band. Figure 4 shows the *fingerprint* of O₂ absorption spectral features at the wavelength region of 759-762 nm which is calculated from the HITRAN database. In order to detect O₂ species in this band, a single mode room-temperature diode laser, which is purchased from Mitsubishi (ML-4405) and emits laser light at 760 nm, was chosen as light source for this monitor system.

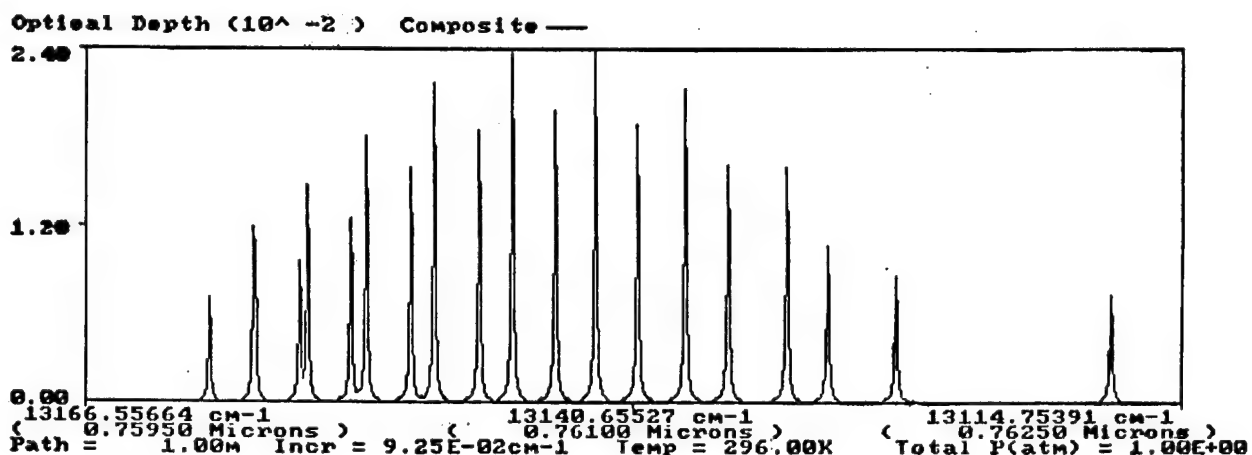


Figure 4. The spectral fringer-print of O₂ absorption lines near the 761 nm wavelength.

In this monitor prototype, 1 meter absorption pathlength is used which corresponds to the situation of 10 optical passes inside the cell. The absorbance of this pathlength with O₂ concentration in air (i.e., ~20.9 %) is 2.4×10^{-2} which is much bigger than a routinely achievable 5×10^{-7} absorbance limit. Even with a single-pass centimeter cell the absorbance of the same O₂ concentration is still much below the achievable detection limit. Therefore, a more compact monitor may be fabricated by considerably reducing the cell physical size.

All the modules including a front panel display and keyboard were integrated into a diode laser frequency modulation spectrometer with its dimensions of 5"x14"x17. The gas sample inlet is connected on the rear panel. In our present design, the unit is constructed for detecting O₂ species. In phase II we plan to develop a system for simultaneously monitoring O₂, CO₂ and NO

gases by adding more diode lasers into the gas cell. Figure 6 (see in APPENDIX section) shows this prototype as well as its interior configuration.

The detection sensitivity, accuracy, and system fluctuations of this prototype were calibrated with a commercial lock-in amplifier (our lock-in amplifier still needs some modifications regarding 2f detection mode) in our laboratory with known O₂ concentration gases. Also the system was tested for its long-time stability (several hundreds hours) and the results are satisfactory for this prototype gas sensor. The performance results are shown in Figure 7 and Figure 8 (see in APPENDIX section), respectively. Figure 7 presents the detection linearity of this prototype. Excellent performance has been achieved in this system. Figure 8 shows detection signal in 5 different data collection runs. The fluctuations of detection signal is very small, about 0.2% in standard deviation. The key features of this prototype are listed as follow:

- Diode Laser: Single mode 3 mW output power @ 760 from Mitsubishi
- Photodetector: Spectral response range from 0.8 - 1.8 μ m from EG&G
- Gas Cell: Custom made with 10 optical passes and total 1 meter pathlength
- Detection Accuracy: 0.04% concentration @ dynamic detection range
- System Stability: 0.5% detection fluctuation over 8 hr.
- Power Consumption: Less than 30 W
- Prototype Size: 5"x14"x17"
- Total Weight: < 20 lb.

4. CONCLUSIONS

In this phase I program, we have successfully demonstrated the feasibility of gas sensor development using the diode laser frequency modulation spectroscopy technique. We have achieved the proposed detection performance from this prototype. Also we have completed the following work:

- Designed, fabricated and evaluated the performances of various electronic modules required for sensor integration.
- Designed and fabricated a custom made multipass cell.
- Integrated all modules into a gas monitor prototype.

- Demonstrated the feasibility of diode laser frequency modulation spectroscopy technique for trace gas monitoring.
- Calibrated the detection performance of this O₂ sensor.

In phase II, by re-designing the sample gas cell and some electronics, we plan to fabricate a more compact medical gas sensor with multiple gas detection ability.

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6. APPENDIX

Figure Captions for Sensor Prototype and Testing Results

Figure 6(a). The exterior view of prototype gas sensor. There is a display window on the left side of front panel. Several digital readings are shown on screen for monitoring the gas pressure inside the cell, the laser working temperature, and detection species concentration. The curve on the screen represents a detection spectrum. Software control commands also are displayed on the right side of the screen.

Figure 6(b). The interior view of the prototype gas sensor. The system power supply is located at the left side of the system. The sample gas cell sits on the right side of the sensor. There are computer, DSP and electronic boards at the center area of the system.

Figure 7. The calibration of O_2 detection of this prototype using known concentration gas. The total gas pressure inside the cell is 761 torr (1 atm.) and the cell temperature is near room temperature. The time constant set in the lock-in amplifier is 1.0 ms.

Figure 8. Stability testing of system detection. The curve consists of five different data collection runs. The big arrow bar represents the detection size with a certain concentration of detection gas.

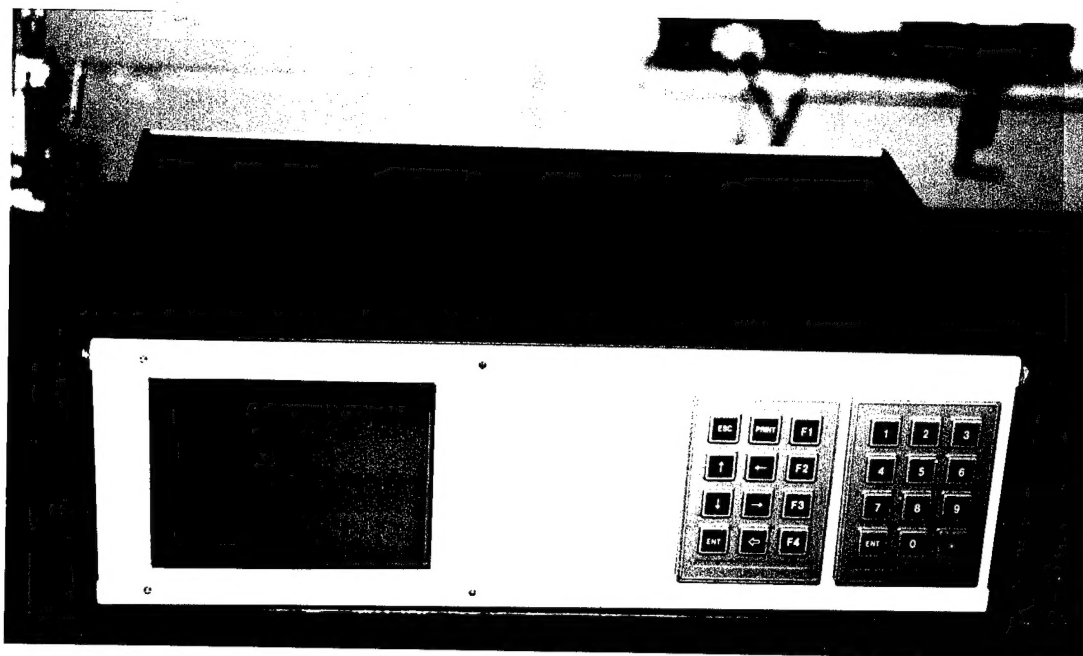


Figure 6(a). The exterior view of prototype gas sensor.

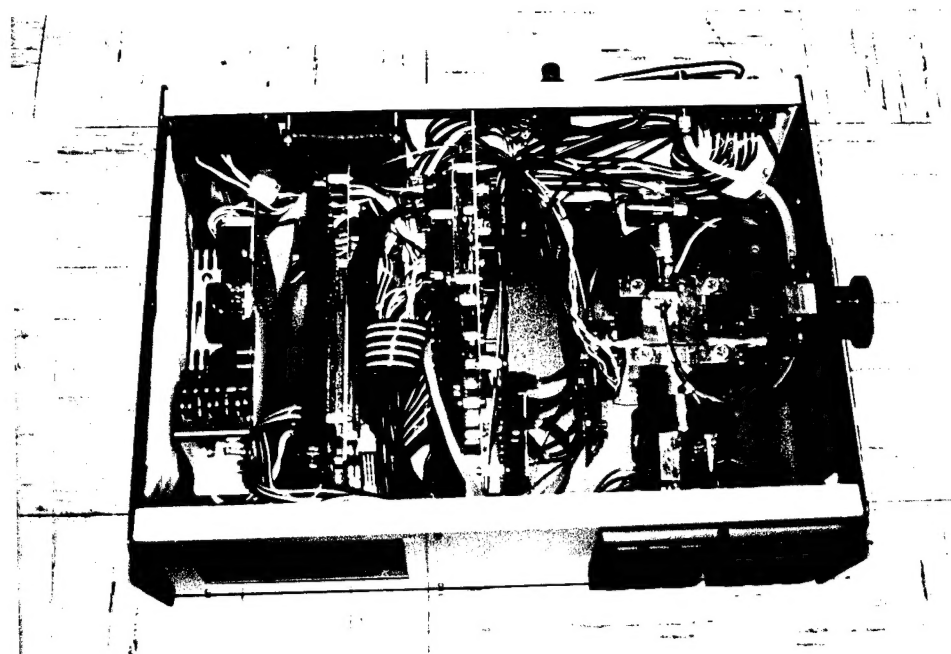


Figure 6(b). The interior view of the prototype gas sensor.

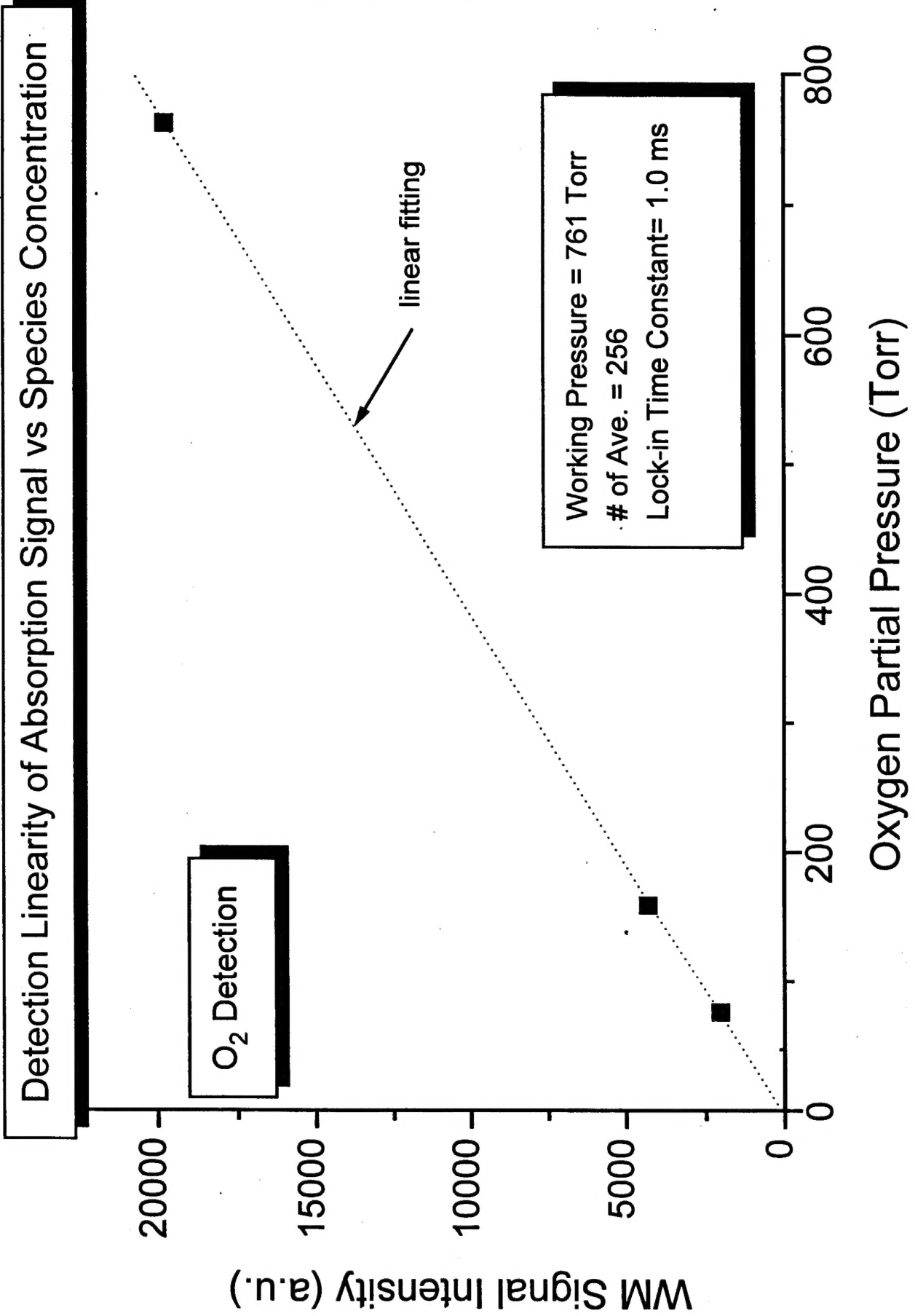


Figure 7. The calibration of O₂ detection of the prototype.

Stability Testing of Diode Laser Based Detection System

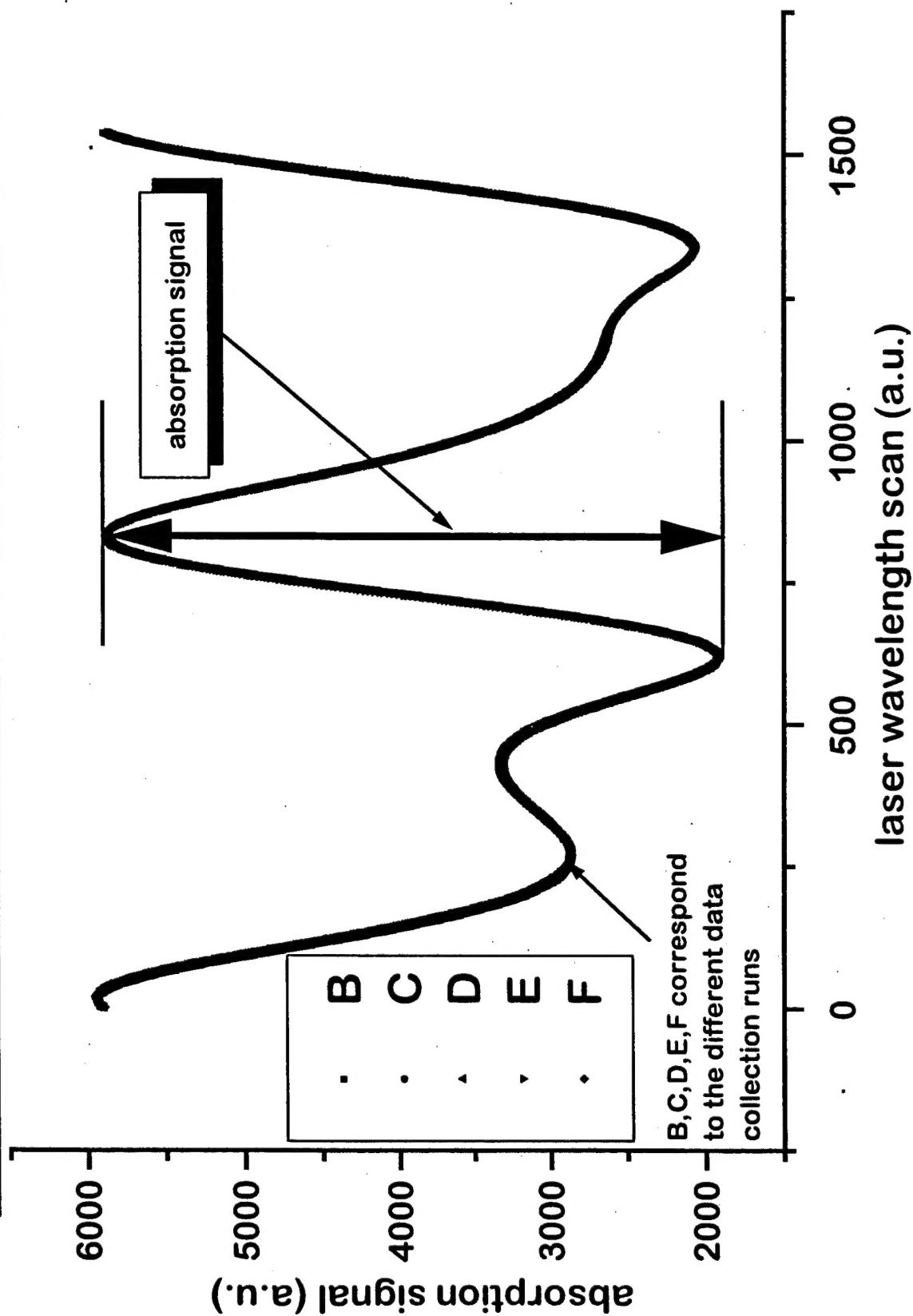


Figure 8. Stability testing of the sensor detection.